THE BIRTH OF CHEMISTRY

IX.

Early Ideas concerning the Process of Combustion.—Association of Nitre with the Air, so far as the part they play in Combustion is concerned.—Hooke's Theory of Combustion.—Mayow's Experiments.—Early Pneumatic Chemistry.—Proof of the Analogy existing between Combustion and Respiration.

AS in the history of matter we find molecules grouping themselves around a common centre or a common line, thus constituting crystalline bodies, so in the history of sciences and of nations we may often observe well-defined axes, about which the facts of particular epochs congregate. Such axes are to be found in the history of chemistry. At the particular period of which we now write, the facts of the science mainly grouped themselves around theories connected with combustion, which involved as collateral matters conceptions regarding the nature of calcination, and of the air.

Combustion was, and still is, the most prominent exhibition of chemical force, with which man ordinarily comes into contact. It is a purely chemical action—the union of dissimilar bodies under the influence of chemical affinity, attended by the evolution of light and heat. Many attempts were made to explain its cause. Fire, in common with earth, air, and water, as we have before seen, was regarded as an element, till almost within our own memory. Epicurus regarded heat as a congeries of minute spherical particles possessing rapid motion, and readily insinuating themselves into the densest bodies. Fire was simply an intense form of heat. Cardanus speaks of flame as *aer accensus*, and of fire as heat immensely augmented. During the Middle Ages the existence of two kinds of fire was admitted—the one pure celestial fire "*subtilis ignis*," "*cœlestis ignis*," the principle or essence of fire; the other "gross earthly fire," or "mundane fire." The latter was the *materia*, the former the *forma*. Celestial fire became mundane fire when it was associated with combustible bodies, that is, in ordinary combustion. Seneca tells us that the Egyptians divided each element into an active and a passive form; fire became active flame which burns, and comparatively passive warmth and light. The elemental nature of fire was not universally admitted during the Middle Ages; thus Francis Bacon asserts, in the *Novum Organum*, that fire is "merely compounded of the conjunction of light and heat in any substance," and he defines heat as a rapid motion of material particles. Athanasius Kircher, in his ponderous treatise, "*Ars Magna Lucis et Umbræ*," affirms that fire is air which is caused to glow by the violent collision of bodies, by which means combustible bodies become flame. At an early date it was observed that fire cannot exist without air; the experiment of burning a candle in a closed vessel was well known. Some affirmed that "air is the food of fire," some that "air nourishes fire." The influence of a blast of air upon fire was well recognised; we have seen that bellows were known at a very early date. When nitre—which for many centuries was one of the most important bodies in chemistry—came to be known, it was soon noticed that it produces intense ignition; that, in fact, to direct a blast of air upon a red-hot coal, or to throw some nitre upon it, produced the same result, viz. greatly augmented combustion. Hence arose the idea that nitre and the air are in some way connected, for "things which are equal to the same are equal to each other." This association of ideas may seem crude to us now, yet we must remember that nitre produces rapid combustion simply because it contains a great quantity of that constituent of the air, oxygen gas, which ordinarily produces combustion. Thus the old natural philosophers, wandering in the dim twilight of experimental knowledge, were not so far wrong in their supposition. The idea mentioned above was very prevalent two centuries ago: Robert Boyle speaks of the presence of a "volatile nitre" in the air; Lord Bacon says that nitre contains a "volatile, crude, and windy spirit"; Clark attributed thunder and lightning to the presence of nitre in the air; Gassendi imagined that minute particles of nitre are diffused throughout the atmosphere. When we heat lead or tin in a current of air, these metals are respectively converted into a powder, or *calx*, and calcination was one of the most important processes in old chemistry. Calcination seemed to be due more or less directly to the air; and metals could also be calcined by heating them with nitre, or with the spirit of nitre—nitric acid; hence arose another bond of connection between nitre and the air; at least, they had something in common. Lemery in his "Cour de Chimie," published in 1675, affirms that the acid of nitre contains a number of "*corpuscules ignées*" locked up in it, and he defines these latter as "a subtle matter, which having been thrown into a very rapid motion, still retains the power of moving with impetuosity, even when it is enclosed in grosser matter; and when it finds some bodies which by their texture or figure are apt to be put into motion, it drives them about so strongly that, their parts rubbing violently against each other, heat is thereby produced."

Thus recognising the causes which had led to the association of the air with nitre, at least so far as they are both concerned in the production of combustion, we are prepared to examine Robert Hooke's theory of combustion. The announcement of this theory marks an important history in the theory of chemistry; it was the first chemical theory worthy of the name, and it gave a far more just and accurate explanation of combustion than the crude and over-belauded theory of Phlogiston, of Beccher and Stahl. Hooke's theory was, moreover, founded upon experiment, and although unfortunately he does not describe the experiments, we see at a glance that it could not have been constructed without such means. "This hypothesis," he writes, "I have endeavoured to raise from an infinity of observations and experiments," and all who know Hooke's writings, are well aware how good an experimenter he was. The theory was published in 1665 in Hooke's "*Micrographia*;" it is there found (Observation 16) buried in a mass of irrelevant matter, and to this cause may, perhaps, to some extent be attributed the fact that it has been so little recognised and known. The theory is stated in twelve propositions, the principal of which are as follows:—

1. That the air is the "universal dissolvent of all sulphureous bodies."

Sulphur was long regarded as the type of combustible bodies, on account of its ready inflammability; some even derive the name from *sal*, πῦρ, the salt of fire. By sulphureous bodies, Hooke simply meant combustible bodies, viz. bodies that can burn in a supporter of combustion. By air being the "universal dissolvent," he meant that through the agency of air combustible bodies are caused to become transformed into similarly invisible substances. For instance, we burn a pound of wood, and a few grains of ash remain, the rest has disappeared into air; as we say now, it has been converted into carbonic anhydride gas; as Hooke said then, it has been dissolved by the air.

2. "That this action it (the air) performs not until the body be sufficiently heated."

In more modern phraseology, every combustible possesses its special igniting point, phosphorus 92° F., sulphur 482° F., and so on.

3. "That this action of dissolution produces or generates a very great heat, and that which we call *Fire*."

4. "That this action is performed with so great a violence, and does so minutely act, and rapidly agitate the smallest parts of the combustible matter, that it produces in the diaphanous medium of the air the action, or pulse, of *Light*.

This would seem to indicate that Hooke considered light to be an intensified form of heat, and to be generated in the same manner, and to be a kind of very rapid motion.

5. "That the dissolution of sulphurous bodies is made by a substance inherent and mixed with the air, that is like, if not the very same with, that which is fixed in saltpetre."

Hooke had evidently traced the connection between certain actions produced by the air and by saltpetre or nitre; and he says it may be readily demonstrated that combustion is effected by that constituent of the air which is fixed in saltpetre. This is a remarkable assertion, because oxygen gas was not discovered until more than a century after the proposition of Hooke's theory; and we now know that nitre contains "fixed" in it the same substance—oxygen gas—which causes air to "dissolve" combustible bodies. It is probable that the connection between air and nitre may have been rendered the more probable in the minds of Hooke and his contemporaries by the knowledge that gunpowder will burn in a space devoid of air; thus, if sulphur and charcoal burn in air, and consume air in burning, and if nitre will cause them to burn out of contact with air it would surely appear that nitre must contain air, or one of its components.

10. "That the dissolving parts of the air are but few, ... whereas saltpetre is a menstruum, when melted and red hot, that abounds more with these dissolvent particles, and therefore as a small quantity of it will dissolve a great sulphureous body, so will the dissolution be very quick and violent."

It was well known that if a piece of red-hot charcoal be thrown into melted nitre, it is consumed with great rapidity, while in the air it burns with far less readiness; hence Hooke infers that that particular component of air which causes it to support combustion exists in a condensed form in saltpetre. He also remarks that if air be violently forced upon a piece of ignited charcoal by bellows it may be made to burn almost as rapidly as in melted nitre.

12. "It seems reasonable to think that there is no such thing as an *element of fire* . . . . but that that shining transient body called *flame* is nothing else but a mixture of air and volatile sulphureous parts of dissoluble or combustible bodies."

Hooke asserts that this theory had been worked out by him several years earlier, and had been well supported by experimental means; he says, moreover, that he has here "only time to hint an hypothesis, which, if God permit me life and opportunity, I may elsewhere prosecute, improve and publish." This he never did; but a young Oxford physician named John Mayow (b. 1645 d. 1679) eagerly accepted the theory, and adduced many experiments in support of it. Perhaps Mayow may have worked with Hooke, during his residence in Oxford, and may have helped to adduce verifications of the then half-formed theory. Mayow's experiments are contained in a treatise entitled—"*Tractatus Quinque Medico-Physici quorum primus agit de Sal-nitro et Spiritu Nitro-aëreo, Secundus de Respiratione* . . . . Oxonii, 1674." The book is altogether important, because the experiments which it contains form the basis of pneumatic chemistry, that is the chemistry of gaseous bodies; it is also distinguished by accurate reasoning and well-founded generalisations. Had it been better known, it can scarcely be doubted that the discovery of oxygen and of various gases made a century ago, would have been forestalled by many years.

FIG. 18.—John Mayow.
(From his "Tractatus Quinque Medico-Physici, 1674.")

Mayow calls the "dissolving parts" of the air and of nitre, which we now call oxygen gas, by the several names of *nitre air*, *fire-air*, and *nitro aerial spirit*. Air does not consist wholly of nitre-air, because when a candle is burnt in a closed vessel only a portion of the contained air is consumed Nitre-air exists in large quantities in a condensed form in nitre; hence combustible bodies mixed with nitre will burn under water, or in a vacuum. The acid of nitre contains all the nitre-air in nitre, but it does not inflame bodies so readily as nitre because in it the nitre-air is surrounded by particles of water which tend to quench the burning body. Nitre-air is not combustible itself, neither does nitre contain any combustible substance, because it may be fused in a red-hot crucible, but no ignition will be observed to take place, until a combustible body has been added. All acids contain nitre-air:—how curiously this contrasts with Lavoisier's name *oxygen*, from οξυς γενναω, which he gave to the gas, because he believed it to be an essential constituent of all acids. Sulphuric acid, according to Mayow, consists of nitre-air united with sulphur; wines become sour and are changed into vinegar by the absorption of nitre-air from the atmosphere. It is the cause also of fermentation and putrefaction, and for this reason, substances when covered with fat or oil do not putrefy. During calcination metals increase in weight, and this increase is attributed by Mayow to absorption of nitric air; thus calx of antimony is antimony *plus* nitre-air, and this is borne out by the fact that a substance absolutely similar to calx of antimony may be procured by treating the metal with the acid of nitre and evaporating Again, rust of iron is iron united with nitre-air.

We come now to some of the first experiments in Pneumatic Chemistry. In one of his experiments Mayow supported a kind of ledge within a bell-jar full of air (see Fig. 19); upon the ledge he placed a piece of camphor, and fired it by concentrating the rays of the sun by a lens upon it. The camphor ignited and burnt for some time, water then rose in the jar; and on again attempting to ignite the camphor he was unsuccessful. A lighted candle was also burned in the jar with the same result. Thus a part only of the air had been consumed, and the remainder was unable to support combustion. The siphon tube (shown on the right-hand side of the figure) was inserted at the commencement in order to render the height of the water the same, inside and outside the tube, as stoppered air jars were then unknown.

Thus it was clearly proved that air is diminished in bulk by combustion. In order to prove that respiration produces a similar result, Mayow tied a piece of moist bladder over the mouth of a jar (Fig 20), and upon this he pressed a cupping-glass, so that the edges fitted air tight Within the cupping-glass he placed a mouse, and as the animal continued to breathe he noticed that the bladder was forced up, more and more into the cupping-glass, proving that the air within it had been diminished by the respiration. Thus Mayow endeavoured to establish a connection between combustion and respiration. He also placed a mouse in a vessel standing over water, and noticed that the water rose in the jar as the respiration continued; and he found it impossible to ignite a combustible body in a jar of air in which a mouse had died. Again, he placed a mouse and a lighted candle together in a jar of air, and he noticed that the mouse only lived half as long as a mouse lived in the same bulk of air without the candle. Air deprived of its nitre-air was assumed to be lighter than nitre-air, because if a mouse is placed near the top of a closed vessel, it dies sooner than if placed near the bottom.

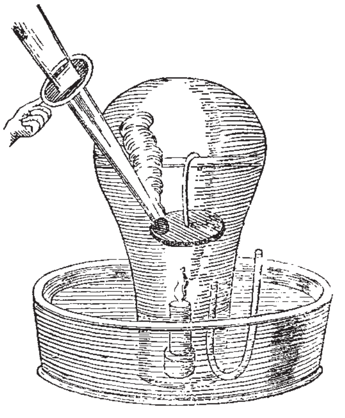

FIG. 19.

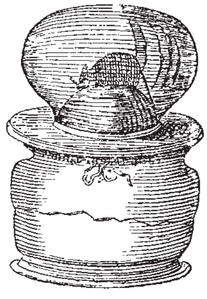

FIG. 20.

Fig. 19.—Early experiment in pneumatic chemistry. Fig. 20.—Early experiment in physiological chemistry.

In 1672 Robert Boyle procured hydrogen gas by acting upon iron filings with an acid, and proved its inflammability; but he does not appear to have further studied its properties, and its discovery is always attributed to Cavendish, a century later. Boyle suggests that it probably consists of "the volatile, sulphur of Mars, or of metalline steams participating in a sulphurous nature." Mayow also procured some of this gas by acting upon iron with dilute sulphuric acid, and he proves that it is not a supporter of life.

Mayow's second treatise is on respiration, and he herein expresses views far in advance of any of his predecessors. He proved that the nitre-air is alone concerned in respiration, and he asserts that this is absorbed by the blood, while the rest is rejected. It unites with combustible particles in the lungs, and thus produces animal heat. The lungs consist of a number of minute sack shaped membranes through which the nitre-air passes to the blood.

We add the following *résumé* of Mayow's treatise, and of the position which it ought to occupy in the history of chemistry, from an article which we wrote on the subject a few years ago.

Mayow's work is remarkable in several respects. In it he conclusively proved that respiration and combustion are analogous processes; he upset the four-element theory by demonstrating the compound nature of air; and he recognised oxygen and nitrogen as clearly and almost as notably as they were recognised a hundred years later—the one the supporter of life and combustion, the principle of acidity, and the cause of fermentation and putrefaction, heavier than atmospheric air; the other incapable of supporting life or combustion, and lighter than atmospheric air. We find, moreover, in this work the dawn of the idea of chemical affinity in the *fermentation*, which he speaks of as taking place between nitre-air and combustible particles, and extending to the production or destruction of things. Mayow even employs some of the terms in general use in the present day; thus he speaks of *affinitas*, existing between acids, and earthy substances, and uses the words *combinetur* and *combinentur* in speaking of the *congressus* of different substances.

The treatise is characterised by much clear and condensed thought, well-sustained argument, and accurate reasoning; moreover, we seldom meet with instances of too hasty generalisation, always the dominant source of error in the early development of a science. We further observe a great advance towards that exact and discriminative mode of thought which is necessary for the investigation of chemical phenomena. The period in which Mayow wrote, was, as regards chemistry, a period of transition; there was as yet no work on scientific chemistry, yet Mayow's treatise approached more nearly to such a work than that of any of his predecessors. The works of previous writers in this direction belonged to one of the three following classes: they were either chemico-metallurgic, chemico-medical, or alchemical treatises, or they partook of the nature of all three. The publication of works on alchemy was fast waning before the advances of the new philosophy; for as superstition retreated, and as men began to devote their energies to the legitimate investigation of nature, a false and chimerical art must of necessity cease to find votaries. Mayow was the first to discuss the intimate nature of an intangible body; other writers had treated of the air as a whole, but no one had endeavoured to ascertain the nature of its internal constitution, or to determine why it produces certain changes in surrounding bodies, upon what these changes depend, and the nature of the constituent or constituents of the air producing them. The old dogma of the elemental nature of the air was received as an absolute truth, although entirely unproven; it was thought that a theory which had been received since the earliest ages must of necessity be correct, and no attempt was made to disprove it.

We see from the above that it was the investigation of the nature of nitre which led to the knowledge of the constitution of the air, and to the first experiments in pneumatic chemistry. Mayow remarks at the commencement of his treatise, that so much had been written about nitre, that it would appear "*ut sal hoc admirabile non minus in philosophia, quam bello strepitus ederet; omniaque sonitu suo impleret;*" and when he remembers its connection with the foregoing results we are almost inclined to agree with him.

G. F. RODWELL

SCIENTIFIC SERIALS

THE *Journal of Botany* for April commences with two useful papers on Cornish botany: Supplementary Contributions to the Flora of North Cornwall, a very little known district, by Mr. J. G. Baker, and another by Mr. T. Archer Briggs.—Mr. F. E. Kitchener contributes a very interesting note on Cross-fertilisation, as aided by sensitive motion, in Musk and Achimenes, the former from observations of his own, the latter from those of Miss Dowson. The structure and motion of the sexual organs, which have long been known in both these flowers, are clearly shown to be contrivances for ensuring cross-fertilisation by insect-agency.—Dr. M'Nab, in a short paper, suggests the employment of the term "pseudocarp," to distinguish fruit-like structures from true fruits, such, for instance, as the apple, the strawberry, the rose-hip, the mulberry, and the fig, into the composition of which other organs besides the true fruit enter. Among the short notes, the most interesting is one of the discovery of *Echium plantagineum* in Cornwall, by M. Ralfs, the plant having been hitherto confined, as far as British botany is concerned, to the Channel Islands. There is a coloured illustration of four new Hymenomycetous fungi, by Mr. W. G. Smith.

Poggendorff's Annalen, No. 1, 1873.—This number opens with the fourth of a series of papers, by Oscar Emil Meyer, on the internal friction of gases; he shows that Poiseuille's law for droppable fluids is verified for gaseous transpiration through narrow pipes.—Dr. Hermann Herwig communicates an account of experiments made on the action of the induction spark in explosion of gaseous mixtures; this action varying with pressure and concentration in the mixture, and with the quantity of electricity passed.—An apparatus of physiological interest, termed the Physometer, is described by P. Hartwig. It is a refinement on Robert Boyle's idea for examining the action of the swimming bladder in fish. The fish, enclosed in a wire cage, is elevated or depressed at will in a vessel filled with water, while the changes of volume in the animal are indicated by the rise and fall of water in a thin tube connected with the vessel.—Dr. Pfeffer, in a paper on the decomposition of carbonic acid in plants by the different spectral rays, infers from his experiments that the curve representing the decomposition mainly corresponds with the curve of brightness.—This paper is followed by another on a similar subject, by E. Gerland. Among the remaining articles may be noted those on the Synaphy (or cohesion) of ethers, by Dr. Scholz, on the polarisation and colour of light reflected in the atmosphere, by E. Hagenbach, and on the electromotive force of very thin gaseous layers on metallic plates, by F. Kohlrausch.

No. 2 contains one of a series of papers, by Julius Thomsen, entitled *Thermo-chemische Untersuchungen*. In the present number he investigates the affinity of hydrogen to the metalloids, chlorine, bromine, and iodine.—Oscar Meyer also continues his series on internal friction of gases; giving a detailed account of two kinds of apparatus for estimating the influence of temperature on friction, and adding some valuable observations on the dynamical theory of gases.—Several new apparatuses are described in this number, Prof. Mayer, of Hoboken, explaining a method of observing the phases and wave-lengths of sound-vibrations in air, and also his acoustic pyrometer based on this method; while an improved deep-sea thermometer, a new form of siphon, and a photometer based on the perception of relief, are described by their several inventors.—A second paper on the physometer is also communicated by P. Hartwig, in which the physiological and other applications of the instrument are more fully discussed.—W. Feddersen contributes an account of a phenomenon which he proposes to call *thermo-diffusion*, and which occurs when two portions of gas are separated by a porous diaphragm, the opposite sides of which have different temperatures. A diffusion is observed which, unlike the ordinary diffusion, takes place when, on both sides of the diaphragm, there is the same gas with the same pressure.—Dr. Morton communicates a note on fluorescence, supplementary to Hagenbach's researches; and there are, in addition, a few notes from English and other sources.

Revue des Sciences Naturelles, Nos. 1-3, 1872.—This new quarterly journal, published at Montpellier, is another proof of the scientific activity which is now reviving in France. Like Lacage Duthier's *Archives de Zoologie*, this provincial review will we trust exhibit what Prof. Jourdain calls in one of these numbers "ces qualités éminemment françaises: la méthode, la rigueur et la clarté," combined with *Deutscher Fleiss und Unbefangenheit*, which though of late years less common in France may well be reclaimed as no alien virtues by the countrymen of Descartes, and Cuvier, and Laennec. The editor is M. Dubrueil, with whom Dr. Heckel was associated in the first two numbers. Among the contributors are the names of Aniouard, Barthélemy, Boyer, Paul Gervais, Joly, Jourdain, Robin, Malinowsky. The first number opens with a paper by Prof. Joly, on the development of the Axolotl, illustrated with some good drawings. There follows a short communication on a new French mollusk (*Pisidia Dubrueui*), an introductory lecture on botany, and an account of the geology of